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Thermal Shrinkage and Change in Chain Conformation of Polypropylene Fibers in Several Solvents and in Air by Partial Melting of Crystalline Regions (Special Issue on Polymer Chemistry X)

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CITATION:

Tanaka, Nobuyuki ...[et al]. Thermal Shrinkage and Change in Chain Conformation of Polypropylene Fibers in Several Solvents and in Air by Partial Melting of Crystalline Regions (Special Issue on Polymer Chemistry X). Bulletin of the Institute for Chemical Research, Kyoto University 1973, 51(2): 81-90

ISSUE DATE:

1973-08-06

URL:

<http://hdl.handle.net/2433/76482>

RIGHT:

Thermal Shrinkage and Change in Chain Conformation of Polypropylene Fibers in Several Solvents and in Air by Partial Melting of Crystalline Regions

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Received February 12, 1973

The thermal shrinkage and the change in chain conformation of polypropylene fibers in several solvents and in air by partial melting of crystalline regions were discussed according to the theoretical treatments on chain conformations for a Gaussian and a Langevin chain obtained in our previous paper.¹⁾

It was concluded that the amorphous chains of polypropylene fibers were extended perpendicular to the fiber axis in these solvents but loosely folded in air.

INTRODUCTION

The melting behaviors of fibrous, partially crystalline polymers accompanied by the change of sample length may be related to the change in conformational entropy of amorphous chains, which decreases with disappearance of the crystalline regions.²⁾ For example, it seems that the conformational entropy of amorphous chains may be smaller for system with lower melting temperature even when the heat of fusion is higher.

In this paper, relations among the orientation factor, the chain dimension, the conformational free energy of amorphous chains, and the partial melting of crystalline regions for polypropylene fibers in several solvents and in air are discussed according to the theoretical treatments on chain conformations proposed in the previous paper¹⁾ for Gaussian and Langevin chains in the absence of solvent.

EXPERIMENTAL

Sample

For measurements of the thermal shrinkage, polypropylene monofilament (375 D), of which the birefringence is $\Delta n = 0.0339$ and the density at 23°C is $\rho = 0.8845$, was used. The degrees of polymerization, x , of this sample was estimated from the intrinsic viscosity in decalin at 135°C according to the equation $[\eta] = 1.10 \times 10^{-4} M^{0.80}$, and is $x = 4280$.

Measurement of Thermal Shrinkage

The thermal shrinkage of this sample was measured, by suspending a weight of 0.787 mg/d, at a heating rate 0.435°C/min in toluene, *p*-xylene, *n*-octane and cyclohexa-

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none, and the change of the sample length was measured by a displacement meter and recorded on an X-Y recorder.

For polypropylene fiber used here, a value of 4% may be expected⁴⁾ for the relative shrinkage during the fiber manufacturing process. Therefore, the corrected value of S was obtained by adding 4% to the relative shrinkage calculated by using the length (observed value) of the original fiber at room temperature.

RESULTS AND DISCUSSION

Conformational Free Energy of Amorphous Chains in Solvent

The change of Gibbs free energy ΔG accompanied by the partial melting of crystalline regions of polymeric materials in solvent may be expressed⁵⁾ by the following equation

$$\begin{aligned}\Delta G &= \{(h_u - Ts_u) - (h_x - Ts_x) + f(\alpha - 1)\} \\ &= kT \left\{ \frac{v_2'}{x\lambda} + (1 - v_2') - \chi_1(1 - v_2')^2 + \frac{1}{x - \xi + 1} \right\}\end{aligned}\quad (1)$$

h_u : heat of fusion per structural unit

s_u : entropy of fusion per structural unit

h_x : heat of transition per structural unit due to pseudo-cross-links in amorphous regions

s_x : entropy of transition per structural unit due to pseudo-cross-links in amorphous regions

f : force

α : drawing ratio

x : total number of structural units in a polymer chain

λ : amorphous fraction

χ_1 : interaction free energy parameter

v_2' : polymer fraction in amorphous regions

ξ : length of crystallite in number of structural units

In this treatment, the number of segments per structural unit was assumed to be equal to the volume ratio of a structural unit to a solvent molecule.

On the other hand, the relative shrinkage S is expressed⁴⁾ by

$$S = (L_c - L_a)\lambda / L_c \quad (2)$$

where L_a and L_c are the lengths of the sample when it is totally amorphous and in fully oriented crystalline state, respectively.

When x is very large, the last term in the right-handed side of eq. (1) is neglected. Further, the change of Gibbs free energy per mole, $N_A \Delta G$, in which N_A is Avogadro's number, is related⁶⁾ to the conformation factor ϕ by

$$N_A \{(h_u - Ts_u) - (h_x - Ts_x) + f(\alpha - 1)\} = RT \frac{\partial \ln \phi}{\partial n} \quad (3)$$

where n is the number of segments per an amorphous chain. If $\alpha \approx 1$ and the equilibrium melting temperature T_m^0 is given by the equation

Partial Melting and Change in Chain Conformation of Polypropylene

Table I. $N_A h_x$, N_{ASx} and $N_A(h_u - h_x)$ for Polypropylene Fibers in Several Solvents

Solvent	T_m^0 (°C)	$RT_m(\partial \ln \phi / \partial n)$ at $\chi_1=0.5$ (cal/mol)	$N_A h_x$ (cal/mol)	$N_A(h_u - h_x)$ (cal/mol)	N_{ASx} (cal/mol·deg)
Toluene	105	18.48	1798.13	101.87	3.979
<i>p</i> -Xylene	103	19.17	1795.92	104.08	3.974
<i>n</i> -Octane	115	18.12	1786.10	113.90	3.953
Cyclohexanone	122	17.48	1776.94	123.05	3.933
(Air)	172	10.80	1596.25	303.75	3.540

$$(h_u - h_x) / (s_u - s_x) = T_m^0, \quad (4)$$

then we obtain

$$\frac{1}{T} - \frac{1}{T_m^0} = R \frac{\partial \ln \phi}{\partial n} / N_A(h_u - h_x) \quad (5)$$

Further, we have the following equations:

$$N_A h_x = N_A h_u - R \left(\frac{\partial \ln \phi}{\partial n} \right) / (1/T - 1/T_m^0) \quad (6)$$

$$N_{ASx} = N_{ASu} - N_A(h_u - h_x) / T_m^0 \quad (7)$$

$N_A h_x$ and N_{ASx} for polypropylene fibers in several solvents and in air were calculated from eqs. (6) and (7) by using the values⁷⁾ $N_A h_u = 1900$ cal/mol, $N_{ASu} = 4.2$ cal/mol·deg and $T_m^0 = 460.5^\circ\text{K}$, and letting $T = T_m$ (T_m is the melting temperature of polypropylene in a given medium). The numerical values obtained were given in Table I. In which the values of $RT_m(\partial \ln \phi / \partial n)$ were obtained by eqs. (9) and (10). $N_A h_x$ and N_{ASx} for every solvent system were considerably large and in the same order as $N_A h_u$ and N_{ASu} , respectively. However, in the air, $N_A h_x$ and N_{ASx} were rather small compared with those in the solvents. In any case, Table I may denote that molecular chains are packed densely in the amorphous regions.

Conformations of Amorphous Chains in Solvent and in Air

Figures 1 and 2 show the relations between the reciprocal relative shrinkage $1/S$ vs. the reciprocal absolute temperature $1/T$ for polypropylene fibers in several solvents and in air. Thus obtained curves may be regarded as composed of straight line portions expressed by

$$\frac{1}{S} = A \frac{1}{T} - C, \quad (A \text{ and } C \text{ are the constants}) \quad (8)$$

As already discussed in our previous paper,⁵⁾ the shrinkage of polypropylene fibers is elucidated by partial melting of crystalline regions. From eq. (8) and eq. (1) substituted with eq. (2), A and C for every straight line portion are given by

$$A = \frac{xL_c}{(L_c - L_a)v_2'k} \{ (h_u - Ts_u) - (h_x - Ts_x) + f(\alpha - 1) \} \quad (9)$$

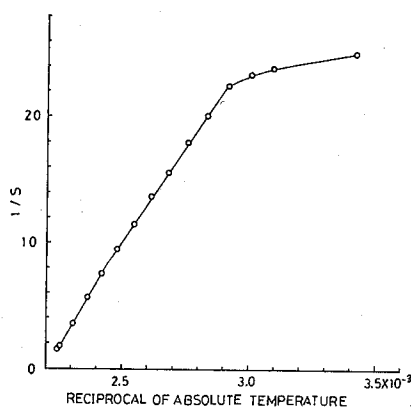


Fig. 1. Relation between the reciprocal relative shrinkage $1/S$ and the reciprocal absolute temperature $1/T$ for polypropylene fibers in air.

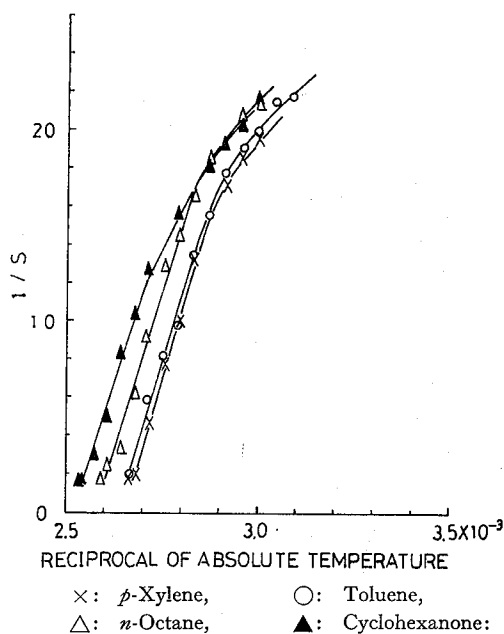


Fig. 2. Relation between $1/S$ and $1/T$ for polypropylene fibers in solvents.

$$C = \frac{xL_c}{(L_c - L_a)v_2'} \left\{ (1 - v_2') - \chi_1(1 - v_2')^2 + \frac{1}{x - \zeta + 1} \right\} \quad (10)$$

Thus, the free energy difference $N_A \Delta G$ and the volume fraction of polymer in amorphous regions v_2' were calculated from eqs. (9) and (10) with measured values of A and C for corresponding temperature ranges (see Table II). As is obvious from Table II, v_2' and $N_A \Delta G$ scarcely depend on the change of λ in every temperature range. Further, the value of $N_A \Delta G$ in solvent at higher temperature range is about 1.7~1.8 times of that in the air.

Partial Melting and Change in Chain Conformation of Polypropylene

Table II. $N_A\Delta G$ and v_2' for Polypropylene Fibers in Several Solvents

Solvent	Temp. Range (°C)	χ_1	δ_s (cal/cm ³) ^{1/2}	v_2'	$N_A\Delta G$ (cal/mol)
(Air)	70-135			1	9.186
	135-172*			1	10.803
<i>n</i> -Octane	75-115*	0	7.80	0.9768	18.122
		0.5		0.9762	18.117
		1.0		0.9759	18.112
<i>p</i> -Xylene	75-103*	0	8.81	0.9744	19.180
		0.5		0.9741	19.173
		1.0		0.9737	19.166
Toluene	75-105*	0	8.94	0.9755	18.488
		0.5		0.9752	18.482
		1.0		0.9749	18.477
Cyclohexanone	80- 95	0	9.92	0.9869	10.823
		0.5		0.9868	10.822
		1.0		0.9868	10.821
	95-122*	0		0.9778	17.486
		0.5		0.9777	17.484
		1.0		0.9773	17.478

* denotes the melting temperature of polypropylene in the solvent.

Also found is that the effect of χ_1 on v_2' and $N_A\Delta G$ is negligibly small in the range of χ_1 between 0 and 1.0.

Figures 3 and 4 show the relation between $N_A\Delta G/T [=R(\partial \ln \phi / \partial n)]$ and the amorphous fraction λ . As is obvious from eq. (1), $N_A\Delta G/T$ decreases with increasing λ .

Next, we will refer to the relation between the chain dimension and the relative shrinkage in solvents and in air for the case $\lambda=1$. The value of S at $\lambda=1$ is represented by¹⁾

$$S(\text{at } \lambda=1) = (L_c - L_a) / L_c = 1 - \sqrt{\langle \cos^2 \gamma \rangle} \quad (11)$$

where γ is the angle between the direction of fiber axis and the direction of a segment. Substitution of eq. (11) in eq. (1) leads to

$$\begin{aligned} \frac{\partial \ln \phi}{\partial n} - (1 - v_2') + \chi_1(1 - v_2')^2 &= \frac{v_2'}{x\lambda} \\ &= \frac{v_2'}{xS} (1 - \sqrt{\langle \cos^2 \gamma \rangle}) \end{aligned} \quad (12)$$

If the direction of fiber axis is the same as that of the end-to-end distance vector, then $\langle \cos^2 \gamma \rangle$ for a Langevin chain is represented by¹⁾

$$\langle \cos^2 \gamma \rangle = 1 - \frac{2 \frac{r}{nb}}{L^* \left(\frac{r}{nb} \right)} \quad (13)$$

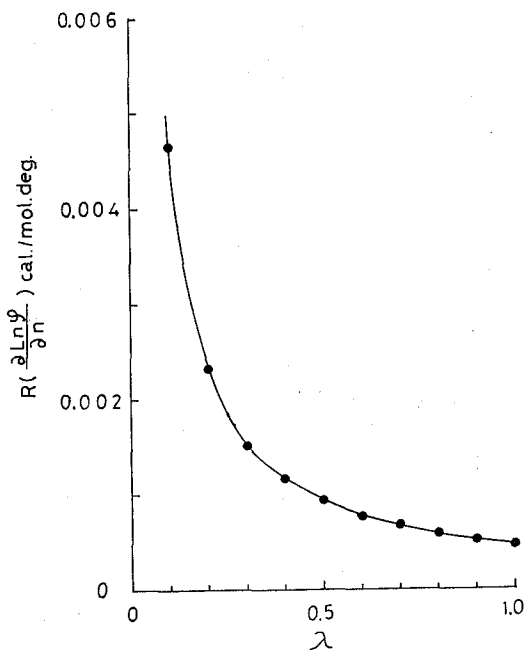


Fig. 3. Relation between $R(\partial \ln \phi / \partial n)$ and the amorphous fraction λ for polypropylene fibers in air.

where,

$$L^*\left(\frac{r}{nb}\right) = 3\frac{r}{nb} + \frac{9}{5}\left(\frac{r}{nb}\right)^3 + \frac{297}{175}\left(\frac{r}{nb}\right)^5 + \dots$$

r : end-to-end distance of an amorphous chain

b : length of a segment

Rearranging eq. (13), $(r/nb)^2$ is approximately represented by

$$\left(\frac{r}{nb}\right)^2 \cong \left(\frac{2}{1 - \langle \cos^2 \gamma \rangle} - 3\right) \frac{5}{9} \quad (14)$$

Further, the orientation factor f_a of the Langevin chain for this case is given by⁷⁾

$$\begin{aligned} f_a &= (3\langle \cos^2 \gamma \rangle - 1) / 2 = 1 - 3(r/nb) / L^*(r/nb) \\ &= \frac{3}{5}(r/nb)^2 + \frac{36}{175}(r/nb)^4 + \frac{108}{875}(r/nb)^6 + \dots \end{aligned} \quad (15)$$

On the other hand, f_a is generally represented by⁸⁾

$$f_a = \{3(L_a/L_c)^2 - 1\} / 2 \quad (16)$$

irrespective of that the direction of the fiber axis is the same or is not the same as that of the end-to-end distance vector. In eq. (16), $L_a = L_c(\langle \cos^2 \gamma \rangle)^{1/2}$.

The sample length is generally written as

$$L = (1 - \lambda)L_c + \lambda \sqrt{\frac{2f_a + 1}{3}} L_c \quad (17)$$

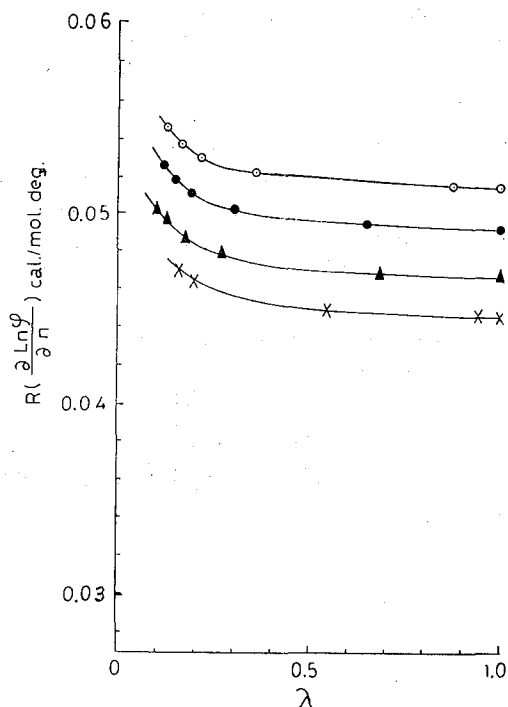


Fig. 4. Relation between $R(\partial \ln \phi / \partial n)$ and the amorphous fraction λ for polypropylene fibers in *p*-xylene (○), toluene (●), *n*-octane (▲), and cyclohexanone (×).

Therefore, Letting f_c be the orientation factor of crystalline chains, the orientation factor f_t of the total chains in the fibers is represented by

$$f_t = (1-\lambda)f_c + \lambda f_a = \{ (L/L_c) - (1-\lambda) \}^2 \left(\frac{3}{2\lambda} \right) + 1 - \frac{3}{2}\lambda \quad (18)$$

Therefore, one obtains

$$L = L_a \quad \text{and} \quad f_t = -0.5 + 1.5(L_a/L_c)^2 = f_a \quad \text{for} \quad \lambda = 1$$

and

$$L = L_c \quad \text{and} \quad f_t = 1 = f_c \quad \text{for} \quad \lambda = 0.$$

Further, when $f_t = 0$, we have

$$L = L_c \sqrt{\lambda^2 - (2/3)\lambda} + (1-\lambda)$$

By using eqs. (11) and (16), numerical values of f_a , γ and $\langle \cos^2 \gamma \rangle^{1/2}$ were calculated. The results obtained were given in Table III.

As seen in Table III, numerical values of f_a in these solvents and in air were negative. In particular, $f_a = -0.4876$ in air is very close to -0.5 , the value assigned when amorphous chains are totally oriented perpendicular to the fiber axis. When the direction of the end-to-end distance vector is the same as that of the fiber axis, the value of f_a for Langevin chain should be $f_a \geq 0$, because $r/nb > 0$ in eq. (15). Accordingly, the chain dimension,

Table III. f_a , γ and $\langle \cos^2 \gamma \rangle^{1/2}$ for Polypropylene Fibers in Several Solvents at $\lambda=1$

Solvent	$1/S$	$1-\langle \cos^2 \gamma \rangle$	f_a	$\langle \cos^2 \gamma \rangle^{1/2}$	γ
Toluene	1.65	0.8448	-0.2672	0.3939	66°48'
<i>p</i> -Xylene	1.64	0.8477	-0.2716	0.3902	67°02'
<i>n</i> -Octane	1.65	0.8448	-0.2672	0.3939	66°48'
Cyclohexanone	1.63	0.8506	-0.2752	0.3865	67°16'
(Air)	1.10	0.9917	-0.4876	0.0909	84°47'

r^2/nb^2 , can not be obtained from eq. (14) so far as f_a is negative, even if amorphous chains are approximated by Langevin chains.

$f_a < 0$ shown in Table III may be attributed to that the direction of the end-to-end distance vector is not in accord with that of the fiber axis.

When both directions are in accord, r/nb for Langevin chain should be positive, and the following inequality should be satisfied

$$\left(\frac{r}{nb}\right)^2 \cong \left\{ \frac{2}{1-\langle \cos^2 \gamma \rangle} - 3 \right\} \left(\frac{5}{9} \right) > 0 \quad (19)$$

or

$$f_a > 0 \quad (20)$$

Therefore, for Langevin chain, the inequalities (21), (22) and (23) are obtained from eq. (19).

$$\langle \cos^2 \gamma \rangle^{1/2} > 0.5773 \quad (21)$$

$$\gamma < 55^\circ 45' \quad (22)$$

$$S = 1 - \langle \cos^2 \gamma \rangle^{1/2} < 0.4227 \quad (23)$$

The experimental values of γ and f_a (Table II) obtained by using eqs. (11) and (16) do not satisfy eqs. (20)~(23).

At this stage, we will calculate f_a , γ and S by using the unperturbed dimension experimentally obtained for polypropylene.^{8,9)} These values were listed in Table IV. It is pointed out that f_a , $\langle \cos^2 \gamma \rangle^{1/2}$, γ , and S given in Table IV satisfy the inequalities (20)~(23).

Now we will proceed the following discussion by assuming that amorphous chains in polypropylene fibers are approximated by Langevin or Gaussian chain, and that the direction of fiber axis is not accord with that of the end-to-end distance vector of the chain. To discuss γ and r^2/nb^2 , we will introduce conditions of partial melting of crystalline regions proposed by Fischer⁶⁾

Table IV. f_a , $\langle \cos^2 \gamma \rangle^{1/2}$, γ , S and $1/S$ for Polypropylene Fibers Calculated from eqs. (14) and (15) for Langevin Chains, and from eq. (11)

Temp. (°C)	r^2/nb^2	r^2/n^2b^2	f_a	$\langle \cos^2 \gamma \rangle^{1/2}$	γ	S	$1/S$
100	15 ⁸⁾	0.0035	0.0021	0.5786	54°14'	0.4214	2.373
125.1	6.35 ⁹⁾	0.0015	0.0009	0.5779	54°42'	0.4221	2.369

For Gaussian chain, in the first place, if partial melting of crystalline regions takes place, then γ should be satisfied⁽⁶⁾ with the following inequality

$$\frac{3}{2n^2b^2}(r^2-nb^2-2rnb\cos\gamma)>0 \quad (24)$$

or

$$\cos\gamma < \frac{r^2-nb^2}{2rnb} \quad (25)$$

This condition for γ is more satisfied with larger r and smaller n . If the amorphous chain is sufficiently extended, eq. (25) is further approximated by

$$\cos\gamma < \frac{1}{2}\left(1-\frac{b}{r}\right) \quad (26)$$

and for $r \gg b$, we have

$$\gamma > 60^\circ$$

Therefore, if γ is smaller than 60° , then partial melting of crystalline regions does not occur but crystallization of amorphous chains is promoted.

For Langevin chain, in the second place, if partial melting of crystalline regions takes place, then γ should be satisfied⁽⁶⁾ with the following inequality

$$-\frac{3}{2n} + \ln\left(\frac{\text{sh } \beta}{\beta}\right) - \beta \cos\gamma > 0 \quad (27)$$

in which

$$\frac{1}{\beta} \cong 1 - \frac{r}{nb} \quad (28)$$

and

$$\ln\left(\frac{\text{sh } \beta}{\beta}\right) \cong \beta - \ln 2\beta \quad (29)$$

Therefore, by using eqs. (28) and (29), eq. (27) is rearranged as

$$1 - \cos\gamma > \left(1 - \frac{r}{nb}\right)\left(\frac{3}{2n} + \ln 2\beta\right) \quad (30)$$

If the molecular chain is sufficiently extended, *i.e.*, $n \sim \frac{r}{b}$, then the right-hand side of eq. (30) becomes 0. Thus, in this case, partial melting takes place at small angle of γ but does not at $\gamma > 60^\circ$.

These two theoretical considerations may lead to that the amorphous chains in polypropylene fibers satisfy the condition to initiate partial melting for Gaussian chain (not for Langevin chain), because γ is larger than 60° (see Table III). This theoretical prediction using Gaussian chain requires $f_a < 0$ for the condition to initiate partial melting, with the direction of end-to-end distance vector different from that of fiber axis (If these two directions are coincided, then f_a should always be positive for both Gaussian and Langevin chain).

For Gaussian chain, $\partial \ln \phi / \partial n$ is related to r by

Table V. r/nb , $(r/nb)^2$ and r^2/nb^2 for Polypropylene Fibers in Several Solvent and in Air with $\lambda=1$

Solvent	r/nb	$(r/nb)^2$	r^2/nb^2	f_a
Toluene	0.8084	0.6535	5598.18	-0.2672
<i>p</i> -Xylene	0.8022	0.6435	5513.02	-0.2716
<i>n</i> -Octane	0.8075	0.6520	5585.76	-0.2672
Cyclohexanone	0.7922	0.6276	5376.15	-0.2752
(Air)	0.2201	0.0484	414.76	-0.4876

$$\frac{\partial \ln \phi}{\partial n} = \frac{3}{2n^2 b^2} (r^2 - nb^2 - 2rnb \cos \gamma) \quad (31)$$

By rearranging eq. (31), we have

$$\frac{r}{nb} = \cos \gamma + \sqrt{\cos^2 \gamma + \frac{1}{n} + \frac{2}{3} \frac{\partial \ln \phi}{\partial n}} \quad (32)$$

$$\begin{aligned} \left(\frac{r}{nb}\right)^2 &= 2 \cos^2 \gamma + \frac{1}{n} + \frac{2}{3} \left(\frac{\partial \ln \phi}{\partial n}\right) \\ &\quad + 2(\cos \gamma) \sqrt{\cos^2 \gamma + \frac{1}{n} + \frac{2}{3} \left(\frac{\partial \ln \phi}{\partial n}\right)} \end{aligned} \quad (33)$$

$$\begin{aligned} \frac{r^2}{nb^2} &= 2n \cos^2 \gamma + 1 + \frac{2n}{3} \left(\frac{\partial \ln \phi}{\partial n}\right) \\ &\quad + 2n(\cos \gamma) \sqrt{\cos^2 \gamma + \frac{1}{n} + \frac{2}{3} \left(\frac{\partial \ln \phi}{\partial n}\right)} \end{aligned} \quad (34)$$

Table V shows the numerical values of r/nb , $(r/nb)^2$ and r^2/nb^2 obtained from eqs. (32)~(34).

In solvent systems, as is obvious from Table V, r/nb , $(r/nb)^2$ and r^2/nb^2 are considerably large in spite of the negative values of f_a . Hence, we conclude that the direction of the end-to-end distance vector does not in accord with that of the fiber axis and the molecular chain may sufficiently extended to the direction vertical to the fiber axis.

On the other hand, f_a value in the air is very close to -0.5 and r/nb value is smaller than that in solvent systems. This may mean that the amorphous chains are loosely folded in the air system.

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